

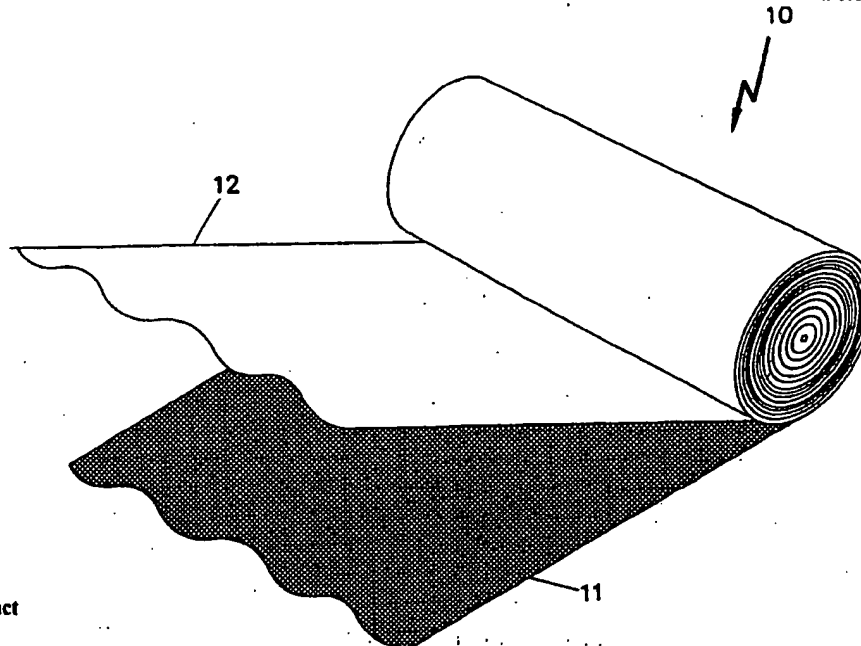
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : <b>B32B 31/20</b>		A1	(11) International Publication Number: <b>WO 91/12136</b>
			(43) International Publication Date: <b>22 August 1991 (22.08.91)</b>
(21) International Application Number: <b>PCT/US91/00463</b>		(74) Agent: ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).	
(22) International Filing Date: <b>23 January 1991 (23.01.91)</b>		(81) Designated States: CA, JP, NL.	
(30) Priority data: 480,982 16 February 1990 (16.02.90) US 569,879 20 August 1990 (20.08.90) US		Published With international search report.	
(71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).		<p><i>Handwritten notes:</i></p> <p>p1 ln 7-37</p> <p>2 22-p3 ln 30</p> <p>p4 n 12-16</p> <p>5 12-16 3-11</p> <p>6-5-p11 ln 23</p> <p>p12</p>	
(72) Inventors: BLAKE, Donald, Lawrence ; 4489 Newton Road, N.E., Newark, OH 43055 (US). DICKSON, Lawrence, Joseph ; 558 Cedar Run Road, Newark, OH 43055 (US). DAWID, Stanley, Anthony, Jr. ; 154 Bolton Avenue, Newark, OH 43055 (US).			

(54) Title: ROLE OF MOLDED, BALLISTIC RESISTANT CLOTH AND METHOD OF MAKING SAME



## (57) Abstract

The present invention provides methods for treating continuous lengths of resin-impregnated sheets (11) so that they can be supplied in roll form, i.e., like a bolt of cloth, for subsequent processing or use. The methods feature the step of winding the continuous length (11) and a separation layer (12) of a material into a roll (10) with the layer separating successive wraps of the continuous length of sheets, followed by a curing step if the resin is a thermosetting resin or by the application of heat and/or pressure otherwise. The continuous lengths optionally may comprise at least one sheet of film, too. The separation layer (12) of material remains separable from the continuous length (11) after treatment. Composite articles made from certain of these continuous lengths are ballistic resistant.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

ROLL OF MOLDED, BALLISTIC RESISTANT CLOTH  
AND METHOD OF MAKING SAME  
BACKGROUND OF THE INVENTION

1. Field of the Invention

This is a continuation-in-part of copending U.S. Serial No. 480,982 filed February 16, 1990.

5 The present invention relates to methods of treating continuous lengths of resin-impregnated sheets so that they can be supplied in roll form, i.e., like a bolt of cloth, for subsequent processing or use. In particular, certain of the treated lengths are useful in flexible hard armor applications, while certain other of the treated lengths are useful in soft armor applications. The present invention also relates to rolls treated in accordance with the methods.

2. Prior Art

15 Ballistic resistant articles such as bulletproof vests, helmets, hard and soft armor, structural members of helicopters and other military equipment, vehicle panels, briefcases, raincoats and umbrellas containing high strength fibers are known. 20 Fibers conventionally used in these articles include aramid fibers such as poly(p-phenylene terephthalamide), graphite fibers, nylon fibers, ceramic fibers, glass fibers and the like. For many applications, such as vests or parts of vests, the fibers are used in a woven or 25 knitted fabric. For many of the other applications, the fibers are encapsulated or embedded in a matrix material.

Ballistic-resistant composite articles comprised of networks of high molecular weight polyethylene or polypropylene fibers, and matrices 30 composed of olefin polymers and copolymers, unsaturated polyester resins, epoxy resins, and other resins curable below the melting point of the fiber are taught by USP 4 403 012 and USP 4 457 985, hereby incorporated by reference.

35 USP 4 623 574, hereby incorporated by reference, discloses the formation of prepreg sheets comprised of elastomer coated high strength fibers which are

- 2 -

substantially parallel and aligned along a common fiber direction. The patent teaches that the prepreg sheets can be plied together, with successive sheets being rotated relative to the first sheet, to form simple composite materials. These composite materials are of a given size, e.g., 12 x 12 inches (4.7 x 4.7 cm), and are individually molded prior to being sent to the customer who then cuts and fabricates the material into a desired configuration. There would be less waste of material, and thus less expense, if the composite materials could be furnished to the customer in continuous roll form, i.e., like a bolt of cloth, rather than in squares or rectangles. And the continuous length would be much easier to handle if it was molded - in effect, it would drape like a fabric rather than being stiff and awkward to cut. Molding typically takes place with compression or heat; the time required for heat molding, e.g., between heated rolls or plates, is essentially too long to permit the practical in line molding of the material after its formation.

The present invention, which was developed in an attempt to overcome the deficiencies of the prior art, provides a molded composite material in continuous roll form and methods of making same.

#### BRIEF DESCRIPTION OF THE INVENTION

This invention is a method of consolidating a continuous ply of at least two resin-impregnated sheets, comprising the steps of: a. winding the continuous ply and a separation layer of a material into a roll with the layer separating successive wraps of the continuous ply; and b. exposing the roll to a sufficient amount of heat and/or pressure to cause the resin-impregnated sheets to substantially adhere to one another, the material being separable from the continuous ply. The resulting ply can have utility in both the soft and hard armor fields. Depending on the resin matrix used, a consolidated length of sheets may or may not stick to another such length.

- 3 -

Those lengths that do not stick to other lengths are good soft armor candidates while those that do stick to other lengths and are not modified with a film surface or otherwise treated to not stick are poor candidates for soft armor; however, a plurality of these latter lengths could be stacked, heated and pressed to form a hard armor laminate.

The present invention is also a method of consolidating a continuous length comprising at least one resin-impregnated sheet and at least one sheet of film, comprising the steps of: a. winding the continuous length and a separation layer of a material into a roll with the layer separating successive wraps of the continuous length of sheets; and b. exposing the roll to a sufficient amount of heat and pressure to cause the resin-impregnated sheet and the sheet of film to substantially adhere to one another, the separation layer of material being separable from the continuous length of sheets. The resulting consolidated length of sheets can be used in soft armor applications, e.g., as a vest insert. The film surface on one or both sides of the length can be chosen to allow slippage relative to another length. For this embodiment, the impregnated sheet is preferably a network of woven fiber.

In another embodiment, the present invention is a method of treating a continuous length comprising at least one uncured thermosetting resin-impregnated sheet, the length having a thickness and the thermosetting resin having an elongation such that the length of sheet is flexible when the thermosetting resin is cured, comprising the steps of: a. winding the continuous length and a separation layer of a material into a roll with the layer separating successive wraps of the continuous length of sheet, the material being separable from the continuous length of sheet after the thermosetting resin is cured; and b. curing the thermosetting resin. With this method

- 4 -

you can eliminate the film surface of the previous  
embodiments for soft armor applications and achieve about  
a twenty percent weight reduction. The cured  
thermosetting resin would provide the required surface  
5 slippage for soft armor applications.

The present invention also includes the rolls of  
material produced by the methods of this invention.

#### BRIEF DESCRIPTION OF THE DRAWING FIGURE

Figure 1 depicts a molded roll 10 of the  
10 present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

By sheet is meant a shaped article such as a  
film, tape, or a network of fiber or tape, biaxially  
oriented or otherwise, most preferably a network of  
15 fiber.

By fiber is meant an elongate body, the length  
dimension of which is much greater than the transverse  
dimensions of width and thickness. Accordingly, the term  
fiber includes monofilament, multifilament, ribbon, strip,  
20 staple and other forms of chopped or cut fiber and the like  
having regular or irregular cross-sections. Fiber and  
filament are used interchangeably hereafter.

By network is meant tapes or fibers arranged in  
configurations of various types. For example, the  
25 plurality of fibers can be grouped together to form a  
twisted or untwisted yarn. The fibers of yarn may be  
formed as a felt, knitted or woven (plain, basket, satin  
and crow feet weaves, etc.) into a network, fabricated  
into a non-woven fabric (random or ordered orientation),  
30 arranged in a parallel array, layered, or formed into a  
fabric by any of a variety of conventional techniques.  
Similarly, the tapes may be woven into a network,  
fabricated into a nonwoven fabric, arranged in a parallel  
array, or formed into a fabric by any of a variety of  
35 conventional techniques.

In the preferred embodiments of the invention,

- 5 -

the sheet comprises untwisted monofilament yarns which are substantially parallel and unidirectionally aligned to form a uniaxial layer in which a matrix material substantially coats the individual filaments. Although the present invention includes a single such layer (or sheet), two or more of these layers are preferably used to form the continuous length, with each layer rotated with respect to adjacent layers. An example is a five layer length with the second, third, fourth and fifth layers rotated +45°, -45°, 90° and 0° with respect to the first layer. Another, preferred example includes two layers with a 0°/90° layout.

The cross-sections of filaments for use in this invention may vary widely. They may be of circular or of flat or of oblong or of irregular or regular multi-lobal cross-section having one or more regular or irregular lobes projecting from the linear or longitudinal axis of the filament. It is particularly preferred that the filaments be of substantially circular, flat or oblong cross-section, most preferably the former.

The equivalent diameter of the filaments and the thickness of the layer may vary widely. In general, the smaller the equivalent diameter and the thinner the layer, the greater the ballistic protection provided; and conversely, the greater the equivalent diameter of the filament and the greater the thickness of the layers, the lower the ballistic protection provided. The ratio of the thickness of the layer to the equivalent diameter of the filament and the equivalent diameter of the filaments are preferably as set forth in USP 4 916 000, hereby incorporated by reference.

The type of filaments used may vary widely and can be metallic filaments, semi-metallic filaments, inorganic filaments and/or organic filaments. Filaments for use in the practice of this invention are those having a tenacity equal to or greater than about 7 g/d, a tensile modulus equal to or greater than about 150 g/d and an energy-to-break equal to or greater than about 8

- 6 -

- Joules/gram (J/g). Preferred are filaments having a tenacity equal to or greater than about 10 g/d, a tensile modulus equal to or greater than about 200 g/d and an energy-to-break equal to or greater than about 20 J/g.
- 5 More preferred filaments are those having a tenacity equal to or greater than about 15 g/d, a tensile modulus equal to or greater than about 300 g/d and an energy-to-break equal to or greater than about 20 J/g. Particularly preferred filaments are those having a tenacity equal to
- 10 or greater than about 16 g/d, a tensile modulus equal to or greater than about 400 g/d, and an energy-to-break equal to or greater than about 27 J/g. Amongst these particularly preferred embodiments, most preferred are those embodiments in which the tenacity of the filaments
- 15 is equal to or greater than about 22 g/d, the tensile modulus is equal to or greater than about 900 g/d, and the energy-to-break is equal to or greater than about 27 J/g. In the practice of this invention, filaments of choice have a tenacity equal to or greater than about 35 g/d, the
- 20 tensile modulus is equal to or greater than about 1500 g/d and the energy-to-break is equal to or greater than about 50 J/g.

Illustrative of useful organic filaments are those composed of polyesters, polyolefins, polyetheramides, 25 fluoropolymers, polyethers, celluloses, phenolics, polyesteramides, polyurethanes, epoxies, aminoplastics, silicones, polysulfones, polyetherketones, polyetheretherketones, polyesterimides, polyphenylene sulfides, polyether acryl ketones, poly(amideimides), and

30 polyimides. Illustrative of other useful organic filaments are those composed of aramids (aromatic polyamides), such as poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly(2,2,2-trimethyl-hexamethylene terephthalamide), poly(piperazine sebacamide), poly(metaphenylene

35 isophthalamide) (Nomex) and poly(p-phenylene terephthalamide) (Kevlar); aliphatic and cycloaliphatic



- 7 -

- polyamides, such as the copolyamide of 30% hexamethylene diammonium isophthalate and 70% hexamethylene diammonium adipate, the copolyamide of up to 30% bis-(-amidocyclohexyl)methylene, terephthalic acid and
- 5 caprolactam, polyhexamethylene adipamide (nylon 66), poly(butyrolactam) (nylon 4), poly(9-aminononanoic acid) (nylon 9), poly(ε-caprolactam) (nylon 7), poly(ε-capryllactam) (nylon 8), polycaprolactam (nylon 6), poly(p-phenylene terephthalamide), polyhexamethylene
- 10 sebacamide (nylon 6,10), polyaminoundecanamide (nylon 11), polydodecanolactam (nylon 12), polyhexamethylene isophthalamide, polyhexamethylene terephthalamide, polycaproamide, poly(nonamethylene azelamide (nylon 9,9), poly(decamethylene azelamide) (nylon 10,9),
- 15 poly(decamethylene sebacamide) (nylon 10,10), poly[bis-(4-aminocyclohexyl)methane 1,10-decanedicarboxamide] (Qiana) (trans), or combinations thereof; and aliphatic, cycloaliphatic and aromatic polyesters such as poly(1,4-cyclohexylidene dimethyl
- 20 eneterephthalate) cis and trans, poly(ethylene-1,5-naphthalate), poly(ethylene-2,6-naphthalate), poly(1,4-cyclohexane dimethylene terephthalate) (trans), poly(decamethylene terephthalate), poly(ethylene terephthalate), poly(ethylene isophthalate), poly(ethylene
- 25 oxybenzoate), poly(para-hydroxy benzoate), poly(dimethylpropiolactone), poly(decamethylene adipate), poly(ethylene succinate), poly(ethylene azelate), poly(decamethylene sebacate), poly(α,α-dimethylpropiolactone), and the like.
- 30 Also illustrative of useful organic filaments are those of liquid crystalline polymers such as lyotropic liquid crystalline polymers which include polypeptides such as poly γ-benzyl L-glutamate and the like; aromatic polyamides such as poly(1,4-benzamide), poly(chloro-1,4-
- 35 phenylene terephthalamide), poly(1,4-phenylene fumaramide), poly(chloro-1,4-phenylene fumaramide),

- 8 -

- poly(4,4'-benzanilide trans, trans-muconamide),  
poly(1,4-phenylene mesaconamide), poly(1,4-phenylene  
(trans-1,4-cyclohexylene amide), poly(chloro-1,4-  
phenylene) (trans-1,4-cyclohexylene amide),  
5 poly(1,4-phenylene 1,4-dimethyl-trans-1,4-cyclohexylene  
amide), poly(1,4-phenylene 2.5-pyridine amide),  
poly(chloro-1,4-phenylene 2.5-pyridine amide),  
poly(3,3'-dimethyl-4,4'-biphenylene 2.5 pyridine amide),  
poly(1,4-phenylene 4,4'-stilbene amide),  
10 poly(chloro-1,4-phenylene 4,4'-stilbene amide),  
poly(1,4-phenylene 4,4'-azobenzene amide),  
poly(4,4'-azobenzene 4,4'-azobenzene amide), poly(1,4-  
phenylene 4,4'-azoxybenzene amide), poly(4,4'-azobenzene  
4,4'-azoxybenzene amide), poly(1,4-cyclohexylene 4,4'-  
15 azobenzene amide), poly(4,4'-azobenzene terephthal amide),  
poly(3,8-phenanthridinone terephthal amide), poly(4,4'-  
biphenylene terephthal amide), poly(4,4'-biphenylene 4,4'-  
bibenzo amide), poly(1,4-phenylene 4,4'-bibenzo amide),  
poly(1,4-phenylene 4,4'-terephthylene amide), poly(1,4-  
20 phenylene 2,6-naphthal amide), poly(1,5-naphthalene  
terephthal amide), poly(3,3'-dimethyl-4,4-biphenylene  
terephthal amide), poly(3,3'-dimethoxy-4,4'-biphenylene  
terephthal amide), poly(3,3'-dimethoxy-4,4-biphenylene  
4,4'- bibenzo amide) and the like; polyoxamides such as  
25 those derived from 2,2'-dimethyl-4,4'-diamino biphenyl and  
chloro-1,4-phenylene diamine; polyhydrazides such as poly  
chloroterephthalic hydrazide, 2,5-pyridine dicarboxylic  
acid hydrazide) poly(terephthalic hydrazide),  
poly(terephthalic-chloroterephthalic hydrazide) and the  
30 like; poly(amide-hydrazides) such as poly(terephthaloyl  
1,4 amino-benzhydrazide) and those prepared from 4-amino-  
benzhydrazide, oxalic dihydrazide, terephthalic dihydrazide  
and para-aromatic diacid chlorides; polyesters such as  
those of the compositions include poly(oxy-trans-1,4-  
35 cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-  
oxy-1,4-phenyl-eneoxyteraphthaloyl) and poly(oxy-cis-1,4-

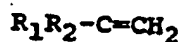
- 9 -

cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl) in methylene chloride-o-cresol poly(oxy-trans-1,4-cyclohexylene oxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-(2-methyl-1,4-phenylene)oxy-  
5 -terephthaloyl) in 1,1,2,2-tetrachloroethane-o-chlorophenol-phenol (60:25:15 vol/vol/vol), poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxy-terephthaloyl] in o-chlorophenol and the like; polyazomethines such  
10 as those prepared from 4,4'-diaminobenzanilide and terephthalaldehyde, methyl-1,4-phenylenediamine and terephthalaldehyde and the like; polyisocyanides such as poly(-phenyl ethyl isocyanide), poly(n-octyl isocyanide) and the like; polyisocyanates such as poly(n-alkyl  
15 isocyanates) as for example poly(n-butyl isocyanate), poly(n-hexyl isocyanate) and the like; lyotropic crystalline polymers with heterocyclic units such as poly(1,4-phenylene-2,6-benzobisthiazole) (PBT), poly(1,4-phenylene-2,6-benzobisoxazole) (PBO), poly(1,4-phenylene-  
20 1,3,4-oxadiazole), poly(1,4-phenylene-2,6-benzobisimidazole), poly[2,5(6)-benzimidazole] (AB-PBI), poly[2,6-(1,4-phenylene-4-phenylquinoline) poly[1,1'-(4,4'-biphenylene)-6,6'-bis(4-phenylquinoline)] and the like; polyorganophosphazines such as polyphosphazine,  
25 polybisphenoxyphosphazine, poly[bis(2,2,2'-trifluoroethylene) phosphazine] and the like; metal polymers such as those derived by condensation of trans-bis(tri-n-butylphosphine)platinum dichloride with a bisacetylene or trans-bis(tri-n-butylphosphine)bis(1,4-butadiynyl)platinum and similar combinations in the  
30 presence of cuprous iodine and an amide; cellulose and cellulose derivatives such as esters of cellulose as for example triacetate cellulose, acetate cellulose, acetate-butyrate cellulose, nitrate cellulose, and sulfate  
35 cellulose, ethers of cellulose as for example, ethyl ether cellulose, hydroxymethyl ether cellulose, hydroxypropyl

- 10 -

ether cellulose, carboxymethyl ether cellulose, ethyl hydroxyethyl ether cellulose, cyanoethylethyl ether cellulose, ether-esters of cellulose as for example acetoxyethyl ether cellulose and benzoyloxypropyl ether cellulose, and urethane cellulose as for example phenyl urethane cellulose; thermotropic liquid crystalline polymers such as celluloses and their derivatives as for example hydroxypropyl cellulose, ethyl cellulose propionoxypropyl cellulose; thermotropic copolyesters as for example copolymers of 6-hydroxy-2-naphthoic acid and p-hydroxy benzoic acid, copolymers of 6-hydroxy-2-naphthoic acid, terephthalic acid and dihydroxybenzophenone, copolymers of phenylterephthalic acid and hydroquinone, copolymers of chlorohydroquinone, terephthalic acid and p-acetoxy cinnamic acid, copolymers of chlorohydroquinone, terephthalic acid and ethylene dioxy-4,4'-dibenzoic acid, copolymers of hydroquinone, methylhydroquinone, p-hydroxybenzoic acid and isophthalic acid, copolymers of (1-phenylethyl)hydroquinone, terephthalic acid and hydroquinone, and copolymers of poly(ethylene terephthalate) and p-hydroxybenzoic acid; and thermotropic polyamides and thermotropic copoly(amide-esters).

Also illustrative of useful organic filaments are those composed of extended chain polymers formed by polymerization of  $\alpha, \beta$ -unsaturated monomers of the formula:



wherein:

$R_1$  and  $R_2$  are the same or different and are hydrogen, hydroxy, halogen, alkylcarbonyl, carboxy, alkoxy carbonyl, heterocycle or alkyl or aryl either unsubstituted or substituted with one or more substituents selected from the group consisting of alkoxy, cyano, hydroxy, alkyl and aryl. Illustrative of such polymers of  $\alpha, \beta$ -unsaturated monomers are polymers including polystyrene, polyethylene, polypropylene,

- 11 -

poly(1-octadecene), polyisobutylene, poly(1-pentene), poly(2-methylstyrene), poly(4-methylstyrene), poly(1-hexene), poly(4-methoxystyrene), poly(5-methyl-1-hexene), poly(4-methylpentene), poly(1-butene), polyvinyl chloride, polybutylene, polyacrylonitrile, poly(methyl pentene-1), poly(vinyl alcohol), poly(vinylacetate), poly(vinyl butyral), poly(vinyl chloride), poly(vinylidene chloride), vinyl chloride-vinyl acetate chloride copolymer, poly(vinylidene fluoride), poly(methyl acrylate), poly(methyl methacrylate), poly(methacrylonitrile), poly(acrylamide), poly(vinyl fluoride), poly(vinyl formal), poly(3-methyl-1-butene), poly(4-methyl-1-butene), poly(4-methyl-1-pentene), poly(1-hexane), poly(5-methyl-1-hexene), poly(1-octadecene), poly(vinyl cyclopentane), poly(vinylcyclohexane), poly( $\alpha$ -vinyl naphthalene), poly(vinyl methyl ether), poly(vinylethylether), poly(vinyl propylether), poly(vinyl carbazole), poly(vinyl pyrrolidone), poly(2-chlorostyrene), poly(4-chlorostyrene), poly(vinyl formate), poly(vinyl butyl ether), poly(vinyl octyl ether), poly(vinyl methyl ketone), poly(methylisopropenyl ketone), poly(4-phenylstyrene) and the like.

Illustrative of useful organic films for use in the present invention are those composed of the polymers described as useful for filaments, above.

Illustrative of useful inorganic filaments for use in the present invention are glass fibers such as fibers formed from quartz, magnesia aluminosilicate, non-alkaline aluminoborosilicate, soda borosilicate, soda silicate, soda lime-aluminosilicate, lead silicate, non-alkaline lead boroalumina, non-alkaline barium boroalumina, non-alkaline zinc boroalumina, non-alkaline iron aluminosilicate, cadmium borate, alumina fibers which include "saffil" fiber in eta, delta, and theta phase form, asbestos, boron, silicone carbide, graphite and

- 12 -

carbon such as those derived from the carbonization of polyethylene, polyvinylalcohol, saran, polyamide (Nomex) type, nylon, polybenzimidazole, polyoxadiazole, polyphenylene, PPR, petroleum and coal pitches  
5 (isotropic), mesophase pitch, cellulose and polyacrylonitrile, ceramic fibers, metal fibers as for example steel, aluminum metal alloys, and the like.

In the preferred embodiments of the invention, the continuous length of sheet is fabricated from an  
10 impregnated filament network, which may include a high molecular weight polyethylene filament, a high molecular weight polypropylene filament, an aramid filament, a high molecular weight polyvinyl alcohol filament, a high molecular weight polyacrylonitrile filament or mixtures  
15 thereof. USP 4 457 985, hereby incorporated by reference, generally discusses such high molecular weight polyethylene and polypropylene filaments. In the case of polyethylene, suitable filaments are those of molecular weight of at least 150,000, preferably at least one  
20 million and more preferably between two million and five million. Such extended chain polyethylene (ECPE) filaments may be grown in solution as described in USP 4 137.394 or USP 4 356 138, or may be a filament spun from a solution to form a gel structure, as described in German  
25 Off. 3 004 699 and GB 20512667, and especially described in U.S. 4 551 296. As used herein, the term polyethylene shall mean a predominantly linear polyethylene material that may contain minor amounts of chain branching or comonomers not exceeding 5 modifying units per 100 main  
30 chain carbon atoms, and that may also contain admixed therewith not more than about 50 weight percent of one or more polymeric additives such as alkene-1-polymers, 1 in particular low density polyethylene, polypropylene or polybutylene, copolymers containing mono-olefins as  
35 primary monomers, oxidized polyolefins, graft polyolefin copolymers and polyoxymethylenes, or low molecular weight

- 13 -

additives such as antioxidants, lubricants, ultraviolet screening agents, colorants and the like which are commonly incorporated by reference. Depending upon the formation technique, the draw ratio and temperatures, and other conditions, a variety of properties can be imparted to these filaments. The tenacity of the filaments should be at least about 8 g/d, preferably at least about 15 g/d, more preferably at least about 25 g/d and most preferably at least about 35 g/d. Similarly, the tensile modulus of the filaments, as measured by an Instron tensile testing machine, is at least about 160 g/d, preferably at least about 500 g/d, more preferably at least about 1000 g/d and most preferably at least about 1500 g/d. The energy-to-break of the filaments is at least about 8 J/g, preferably at least about 25 J/g, more preferably at least about 40 J/g and most preferably at least about 50 J/g. These highest values for tenacity, tensile modulus and energy-to-break are generally obtainable only by employing solution grown or gel filament processes.

Similarly, highly oriented polypropylene of molecular weight at least 200,000, preferably at least one million and more preferably at least two million, may be used. Such high molecular weight polypropylene may be formed into reasonably well oriented filaments by techniques described in the various references referred to above, and especially by the technique of USP's 4 663 101 and 4 784 820 and US Patent Application Serial No. 069 684, filed July 6, 1987 (see published application WO 89 00213). Since polypropylene is a much less crystalline material than polyethylene and contains pendant methyl groups, tenacity values achievable with polypropylene are generally substantially lower than the corresponding values for polyethylene. Accordingly, a suitable tenacity is at least about 8 g/d, preferably at least about 12 g/d, and more preferably at least about 15 g/d. The tensile modulus for polypropylene is at least about 160 g/d,

- 14 -

preferably at least about 250 g/d, and more preferably at least about 300 g/d. The energy-to-break of the polypropylene is at least about 8 J/g, preferably at least about 40 J/g, and most preferably at least about 60 J/g.

5 High molecular weight polyvinyl alcohol filaments having high tensile modulus are described in USP 4 440 711, hereby incorporated by reference. Preferred polyvinyl alcohol filaments will have a tenacity of at least about 7 g/d, a modulus of at least about 150 g/d and  
10 an energy-to-break of at least about 8 J/g, and particularly preferred PV-OH filaments will have a tenacity of at least about 15 g/d, a modulus of at least about 300 g/d and an energy-to-break of at least about 25 J/g. Most preferred PV-OH filaments will have a tenacity  
15 of at least about 20 g/d, a modulus of at least about 500 g/d and an energy-to-break of at least about 30 J/g. Suitable PV-OH filament having a weight average molecular weight of at least about 200,000 can be produced, for example, by the process disclosed in USP 4 599 267.

20 In the case of polyacrylonitrile (PAN), PAN filament for use in the present invention are of molecular weight of at least about 400,000. Particularly useful PAN filament should have a tenacity of at least about 7 g/d and an energy-to-break of at least about 8 J/g. PAN  
25 filament having a molecular weight of at least about 400,000, a tenacity of at least about 15 to about 20 g/d and an energy-to-break of at least about 25 to about 30 J/g is most useful in producing ballistic resistant articles. Such filaments are disclosed, for example, in  
30 US 4 535 027.

In the case of aramid filaments, suitable aramid filaments formed principally from aromatic polyamide are described in USP 3 671 542, which is hereby incorporated by reference. The aramid filament will have a tenacity of at  
35 least about 15 g/d, a modulus of at least about 400 g/d and an energy-to-break of at least about 8 J/g. Preferred



- 15 -

aramid filament will have a tenacity of at least about 20 g/d, a tensile modulus of at least about 500 g/d and an energy-to-break at least about 20 J/g, and particularly preferred aramid filaments will have a tenacity of at least about 20 g/d, a modulus of at least about 1000 g/d and an energy-to-break of at least about 20 J/g. Most preferred aramid filaments will have a tenacity of at least about 22 g/d, a modulus of at least about 900 g/d and an energy-to-break of at least about 27 J/g. For example, poly(p-phenylene terephthalamide) filaments produced commercially by Dupont Corporation under the trade name of Kevlar<sup>®</sup> 29, 49, 129 and 149 and having moderately high moduli and tenacity values are particularly useful in forming ballistic resistant composites. Also useful in the practice of this invention is poly(metaphenylene isophthalamide) filaments produced commercially by Dupont under the trade name Nomex.

In the case of liquid crystal copolyesters, suitable filaments are disclosed, for example, in U.S. Patents 3 975 487, 4 118 372, and 4 161 470, hereby incorporated by reference. Tenacities of about 15 to 30 g/d, more preferably about 20 to 25 g/d, modulus of about 500 to 1500 g/d, preferably about 1000 to 1200 g/d, and an energy-to-break of at least about 10 J/g are particularly desirable.

The matrix material employed in the practice of this invention comprises one or more thermosetting resins, or one or more thermoplastic resins, or a blend of such resins. The elongation of the resin/resin system must be greater than that of the reinforcing filament and preferably ranges from about 3 to about 500 percent (ASTM D-638). Resins may be blended in order to achieve higher elongation values, e.g., an epoxy resin (EPON 828, Shell Chemical) with an elongation of about 0.5% may be blended with another epoxy resin (EPON 736, Shell Chemical) having an elongation of about 40% to achieve an epoxy resin

- 16 -

system having an elongation of about 14%. Suitable reinforcing filaments for this system would include, by way of example, glass, aramid, polyethylene, polypropylene, polyvinyl alcohol, polyacrylonitrile or mixtures thereof.

As used herein "thermoplastic resins" are resins which can be heated and softened, cooled and hardened limitless times without undergoing a basic alteration, and "thermosetting resins" are resins which do not tolerate thermal cycling and which cannot be resoftened and reworked after molding, extruding or casting and which attain new, irreversible properties when once set at a temperature which is critical to each resin.

Thermosetting resins useful in the practice of this invention may vary widely. Illustrative of useful thermosetting resins are alkyds such as those derived from esterification of polybasic acids, as for example, phthalic anhydride, fumaric acid, maleic anhydride, isophthalic acid, terephthalic acid, trimesic acid, hemimellitic acid, succinic anhydride, fatty acids derived from mineral or vegetable oils and the like, and polyhydric alcohols as for example glycerol, ethylene glycol, propylene glycol, pinacol, 1,4-butanediol, 1,3-propanediol, sorbitol, pentaerythritol, 1,2-cyclohexanediol and the like. Other useful thermosetting resins are acrylics such as crosslinkable polyacrylics, polyacrylates, epoxydiacrylates, urethane diacrylates and the like. Still other useful thermosetting resins are amino resins derived from reaction between formaldehyde and various amino compounds such as melamine, urea, aniline, ethylene urea, sulfonamide, dicyanodiamide and the like. Other useful thermosetting resins include urethanes derived from reaction of polyisocyanates or diisocyanates such as 2,6-tolylene diisocyanate, 2,4-tolylene diisocyanate, 4,4'-diphenyl-methane diisocyanate, 4,4'-dicyclohexyl-methane diisocyanate and the like, and polyols such as

- 17 -

glycerin, ethylene glycol, diethylene glycol, trimethylolpropane, 1,2,6-hexanetriol, sorbitol, pentaerythritol and the like.

Exemplary of still other thermosetting resins useful in the practice of this invention are unsaturated polyesters derived from reaction of dibasic acids such as maleic anhydride, fumaric acid, adipic acid, azelaic acid and the like, and dihydric alcohols such as ethylene glycol and propylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, diethylene glycol, dipropylene glycols and the like; and silicones such as dimethyldichlorosilane and the like.

Yet another class of useful thermosetting resins are epoxies based on saturated or unsaturated aliphatic, cycloaliphatic, aromatic and heterocyclic epoxides. Useful epoxides include glycidyl ethers derived from epichlorohydrin adducts and polyols, particularly polyhydric phenols. Another useful epoxide is the diglycidyl ether of bisphenol A. Additional examples of useful polyepoxides are resorcinol diglycidyl ether, 3,4-epoxy-6-methylcyclohexylmethyl-9,10-epoxystearate, 1,2-bis(2,3-epoxy-2-methylpropoxy)ethane, diglycidyl ether of 2,2-(p-hydroxyphenyl) propane, butadiene dioxide, dicyclopentadiene dioxide, pentaerythritol tetrakis(3,4-epoxycyclohexanecarboxylate), vinylcyclohexene dioxide, divinylbenzene dioxide, 1,5-pentadiol bis(3,4-epoxycyclohexane carboxylate), ethylene glycol bis(3,4-epoxycyclohexane carboxylate), 2,2-diethyl-1,3-propanediol bis(3,4-epoxycyclohexanecarboxylate), 1,6-hexanediol bis(3,4-epoxycyclohexanecarboxylate), 2-butene-1,4-diol bis(3,4-epoxy-6-methylcyclohexanecarboxylate), 1,1,1-trimethylolpropane tris (3,4-epoxycyclohexanecarboxylate), 1,2,3-propanetriol tris(3,4-epoxycyclohexanecarboxylate), dipropylene glycol bis(2-ethylhexyl-4,5-epoxycyclohexane-1,2-dicarboxylate), diethylene glycol bis(3,4-epoxy-6-methylcyclohexanecarboxylate), triethylene glycol bis(3,4-

- 18 -

- epoxycyclohexanecarboxylate), 3,4-epoxycyclohexylmethyl  
3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-1-  
methylcyclohexylmethyl 3,4-epoxy-1-  
methylcyclohexanecarboxylate, bis(3,4-  
5 epoxycyclohexylmethyl) pimelate, bis(3,4-epoxy-6-  
methylenecyclohexylmethyl) maleate, bis(3,4-epoxy-6-  
methylcyclohexylmethyl) succinate, bis(3,4-  
epoxycyclohexylmethyl) oxalate, bis(3,4-epoxy-6-  
methylcyclohexylmethyl) sebacate, bis(3,4-epoxy-6-  
10 methylcyclohexylmethyl) adipate, bis(3,4-  
epoxycyclohexylmethyl) terephthalate,  
2,2'-sulfonyldiethanol bis(3,4-  
epoxycyclohexanecarboxylate), N,N'-ethylene bis(4,5-  
epoxycyclohexane-1,2-dicarboximide), di(3,4-  
15 epoxycyclohexylmethyl) 1,3-tolylenedicarbamate,  
3,4-epoxy-6-methylcyclohexanecarboxaldehyde acetal,  
3,9-bis(3,4-epoxycyclohexyl) spirobi-(methadioxane), and  
the like.

- Useful thermosetting resins also include  
20 phenolic resins produced by the reaction of phenols and  
aldehydes. Useful phenols include phenol, o-cresol,  
m-cresol, p-cresol, p-tertbutylphenol, p-tertoctylphenol,  
p-nonylphenol, 2,3-xlenol, 2,4-xlenol, 2,5-xlenol,  
2,6-xlenol, 3,1-xlenol, 3,4-xlenol, resorcinol,  
25 bisphenol-A and the like. Useful aldehydes include  
formaldehyde, acetaldehyde, propionaldehyde,  
n-butyraldehyde, isobutyraldehyde, glyoxal,  
furfural and the like.

- Other useful thermosetting resins are aromatic  
30 vinylesters such as the condensation product of epoxide  
resins and unsaturated acids usually diluted in a compound  
having double bond unsaturation such as vinylaromatic  
monomer as for example styrene and vinyltoluene, and  
diallyl phthalate. Illustrative of useful vinylesters are  
35 diglycidyl adipate, diglycidyl isophthalate, di(2,3-  
epoxybutyl) adipate, di(2,3-epoxybutyl) oxalate, di(2,3-

- 19 -

epoxyhexyl) succinate, di(3,4-epoxybutyl) maleate, di(2,3-epoxyoctyl) pimelate, di(2,3-epoxybutyl) phthalate, di(2,3-epoxyoctyl) tetrahydrophthalate, di(4,5-epoxydodecyl) maleate, di(2,3-epoxybutyl) terephthalate, di(2,3-epoxypentyl) thioldipropionate, di(5,6-epoxytetradecyl) diphenyldicarboxylate, di(3,4-epoxyheptyl) sulphonyldibutyrate, tri(2,3-epoxybutyl) 1,2,4 butanetricarboxylate, di(5,6-epoxypentadecyl) maleate, di(2,3-epoxybutyl) azelate, di(3,4-epoxybutyl) citrate, di(5,6-epoxyoctyl) cyclohexane-1,3-dicarboxylate, di(4,5-epoxyoctadecyl) malonate, bisphenol-A-fumaric acid polyester and the like.

Preferred thermosetting resins for use in the practice of this invention are vinylesters, unsaturated polyesters, epoxies and phenolics. Particularly preferred thermosetting resins are vinylesters, epoxies and phenolics, with vinylesters being the thermosetting resin of choice.

Thermoplastic resins for use in the practice of this invention may also vary widely. Illustrative of useful thermoplastic resins are polyactones such as poly(pivalolactone), poly( $\epsilon$ -caprolactone) and the like; polyurethanes derived from reaction of diisocyanates such as 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 4,4'-diphenylisopropylidene diisocyanate, 3,3'-dimethyl-4,4'-diphenyl diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, dianisidine diisocyanate, tolidine diisocyanate, hexamethylene diisocyanate, 4,4'-diisocyananodiphenylmethane and the like and linear long-chain diols such as poly(tetramethylene adipate), poly(ethylene adipate), poly(1,4-butylene adipate), poly(1,5-pentylene adipate), poly(1,3 butylene adipate),

- 20 -

- poly(ethylene succinate), poly(2,3-butylene succinate),  
polyether diols and the like, polycarbonates such as  
poly[methane bis (4-phenyl)carbonate], poly[1,1-ether  
bis(4-phenyl) carbonate], poly[diphenylmethane  
5 bis(4-phenyl) carbonate], poly[1,1-cyclohexane  
bis(4-phenyl)carbonate] and the like; poly sulfones,  
polyether ether ketones, polyamides such as poly(4-amino  
butyric acid), poly(hexamethylene adipamide),  
poly(6-aminohexanoic acid), poly(m-xylylene adipamide),  
10 poly(p-xylylene sebacamide), poly(2,2,2-trimethyl  
hexamethylene terephthalamide), poly(metaphenylene  
isophthalamide) (Nomex), poly(p-phenylene terephthalamide)  
(Kevlar), and the like, polyesters such as poly(ethylene  
azelate), poly(ethylene-1,5-naphthalate, poly(1,4-  
15 cyclohexane dimethylene terephthalate), poly(ethylene  
oxybenzoate) (A-Tell), poly(para-hydroxy benzoate)  
(Ekonol), poly(1,4-cyclohexylidene dimethylene  
terephthalate) (Kodel) (as), poly(1,4-cyclohexylidene  
dimethylene terephthalate) (Kodel) (trans), polyethylene  
20 terephthalate, polybutylene terephthalate and the like;  
poly(arylene oxides) such as poly(2,6-dimethyl-1,4-  
phenylene oxide), poly(2,6-diphenyl-1,4-phenylene oxide)  
and the like; poly(arylene sulfides) such as  
poly(phenylene sulfide) and the like; polyetherimides;  
25 thermoplastic elastomers such as polyurethane elastomers,  
fluoroelastomers, butadiene/acrylonitrile elastomers,  
silicone elastomers, polybutadiene, polyisobutylene,  
ethylene-propylene copolymers, ethylene-propylene-diene  
terpolymers, polychloroprene, polysulfide elastomers,  
30 block copolymers, made up of segments of glassy or  
crystalline blocks such as polystyrene,  
poly(vinyl-toluene), poly(t-butyl styrene), polyester and  
the like and the elastomeric blocks such as polybutadiene,  
polyisoprene, ethylene-propylene copolymers,  
35 ethylene-butylene copolymers, polyether ester and the like  
as for example the copolymers in polystyrene-polybutadiene-

- 21 -

polystyrene block copolymer manufactured by Shell Chemical Company under the trade name of Kraton; vinyl polymers and their copolymers such as polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinyl butyral, polyvinylidene chloride, ethylene-vinyl acetate copolymers, and the like; polyacrylics, polyacrylate and their copolymers such as polyethyl acrylate, poly(n-butyl acrylate), polymethyl methacrylate, polyethyl methacrylate, poly(n-butyl methacrylate), poly(n-propyl methacrylate), polyacrylamide, polyacrylonitrile, polyacrylic acid, ethylene-acrylic acid copolymers, methyl methacrylate-styrene copolymers, ethylene-ethyl acrylate copolymers, methacrylate butadiene-styrene copolymers and the like; polyolefins such as low density polyethylene, polypropylene, chlorinated low density polyethylene, poly(4-methyl-1-pentene) and the like; ionomers; and polyepichlorohydrins.

In the preferred embodiments of the invention, the thermoplastic material is selected from the group consisting of polyurethanes, polyvinyls, polyacrylics, polyolefins, and polyisoprene-polyethylene-butylene-polystyrene or polystyrene-polyisoprene-polystyrene block copolymer thermoplastic elastomers, most preferably the latter.

The proportion of matrix to filament in the composite article is not critical and may vary widely. In general, the matrix material may form from about 10 to about 90% by volume, preferably about 10 to 80%, and most preferably about 10 to 30%.

The continuous lengths/plies of sheets can be fabricated using a number of procedures. In the preferred embodiment, the filaments are precoated with the desired matrix material prior to being arranged in a network. The coating may be applied to the filaments in a variety of ways and any method known to those of skill in the art for coating filaments may be used. The networks produced therefrom are formed into "simple composites," which alone

- 22 -

or with the optional film layer may be the precursor to preparing complex composite articles. By "simple composite" is meant a composite made up of one or more layers, each of the layers containing filaments as  
5 described above with a matrix material which may include minor proportions of other materials such as fillers, lubricants or the like.

Yarn bundles of from about 30 to about 2000 individual filaments of less than about 12 denier, and  
10 more preferably of about 100 individual filaments of less than about 7 denier, are supplied from a creel, and are led through guides and a spreader bar into a collimating comb just prior to coating. The collimating comb aligns the filaments coplanarly and in a substantially parallel,  
15 and unidirectional fashion. The filaments are then sandwiched between release papers, one of which is coated with a wet matrix resin. This system is then passed under a series of pressure rolls to complete the impregnation of the filaments. The top release paper is pulled off and  
20 rolled up on a takeup reel while the impregnated network of filaments proceeds through a heated tunnel oven to remove solvent and then be taken up.

In the most preferred embodiment of this invention, two such impregnated networks are then  
25 continuously cross plied, preferably by cutting one of the networks into lengths that can be placed successively across the width of the other network in a 0°/90° orientation. This forms a continuous ply. This continuous ply, optionally with film as discussed  
30 below, is then wound with a separation layer of material into a roll for treatment.

In another embodiment, one or more uncured thermosetting resin-impregnated networks of filaments are similarly formed into a continuous length for winding with  
35 a separation layer of material into a roll for curing of the resin. In this embodiment, the continuous length must



- 23 -

be of a thickness and the resin must have an elongation such that the continuous length is flexible when the resin is cured.

In yet another embodiment, one or more resin-  
5 impregnated networks of filaments are similarly formed into a continuous length to which at least one sheet of film, as discussed below, is added for winding with a separation layer of material into a roll for treatment.

Film may optionally be used as one or more  
10 layers of the continuous length, preferably as an outer layer. The film, or films, are added after application of the matrix material and formation of a continuous length or ply, as the case may be. The film thickness minimally is about 0.1 mil and may be as large as desired so long as  
15 the length of sheets is still sufficiently flexible to permit roll formation. The preferred film thickness ranges from about 0.1 to 1.0 mil, with about 0.35 to 0.50 mil being preferred.

Films can be used on the surface of the length  
20 (or ply) for a variety of reasons, e.g., to vary frictional properties, to increase flame retardance, to increase chemical resistance, to increase resistance to radiation degradation, and/or to prevent diffusion of material into the matrix. The film may or may not adhere to the  
25 continuous length or ply depending on the choice of film, resin and filament. Heat and/or pressure may cause the desired adherence, or it may be necessary to use an adhesive which is heat or pressure sensitive between the film and the length or ply to cause the desired  
30 adherence. Illustrative adhesives include polystyrene-polyisoprene-polystyrene block copolymer thermoplastic elastomers, thermoplastic and thermosetting polyurethanes, thermoplastic and thermosetting polysulfides, and typical hot melt adhesives such as polyvinyl chloride and the  
35 like. Blends of adhesives can also be used.

Films which may be used in the present invention include thermoplastic polyolefinic films, thermoplastic

- 24 -

elastomeric films, crosslinked thermoplastic films, crosslinked elastomeric films, polyester films, polyamide films, fluorocarbon films, urethane films, polyvinylidene chloride films, polyvinyl chloride films and multilayer  
5 films. Homopolymers or copolymers of these films can be used, and the films may be unoriented, uniaxially oriented or biaxially oriented. The films may include pigments or plasticizers.

Useful thermoplastic polyolefinic films include  
10 those of low density polyethylene, high density polyethylene, linear low density polyethylene, polybutylene, and copolymers of ethylene and propylene which are crystalline.

Polyester films which may be used include those  
15 of polyethylene terephthalate and polybutylene terephthalate.

The separation layer of material which is wrapped into a roll with the continuous ply functions as an interleaf, and as such, must be separable with a  
20 minimum of effort from the continuous length of sheet/ply after heat/pressure treatment. The choice of material for the interleaf may vary depending on what other functions are desired of the material. The interleaf material can be used to supply the necessary pressure, if its tensile  
25 strength is sufficiently high, if tightly wrapped with the continuous length of sheet/ply when forming the roll of material; acceptable materials for this application, by way of example, are waxed (e.g., silicone) paper such as Kraft paper, nylon (e.g., nylon 6) film, or polyester  
30 (e.g., Mylar) film. Pressure can also be applied by an interleaf material made from a plastic film wrap which shrinks when the roll is exposed to heat; acceptable materials for this application, by way of example, are polyester, polyethylene, polyvinyl chloride and  
35 ethylvinylacetate.

The temperatures and/or pressures to which the continuous lengths of sheet/plies of the present invention

- 25 -

are exposed to cure the thermosetting resin or to cause adherence of the networks to each other and optionally, to at least one sheet of film, vary depending upon the particular system used. For example, for extended chain polyethylene filaments, temperatures range from about 20°C. to about 150°C., preferably from about 80°C. to about 145°C., more preferably from about 100°C. to about 135°C, depending on the type of matrix material selected. The pressures may range from about 10 psi (69 kPa) to about 10,000 psi (69,000 kPa). Pressures from about 100 psi (690 kPa) to about 10,000 psi (69,000 kPa), when coupled with temperatures in the range of about 150°C. to about 155°C for a time of between 1 to 5 min., may cause the film, if any, to become translucent or transparent. For polypropylene filaments, the upper limitation of the temperature range would be about 10 to about 20°C. higher than for ECPE filament. For aramid filaments, especially Kevlar filaments, the temperature range would be about 149 to 205°C. (about 300 to 400°F.).

Pressure may be applied to the roll in a variety of ways. Shrink wrapping with plastic film wrap as the interleaf and tightly wrapping with an interleaf having sufficient tensile strength are mentioned above. Autoclaving is another way of applying pressure, in this case simultaneous with the application of heat. The exterior of the roll may be wrapped with a heat shrinkable material or the entire roll can be placed in a heat shrinkable bag and then be exposed to temperatures which will shrink wrap the material/bag, and thus apply pressure to the roll.

Many of the rolls formed with continuous lengths of sheet/plies utilizing elastomeric resin systems, thermosetting resin systems, or resin systems wherein a thermoplastic resin is combined with an elastomeric or thermosetting resin can be treated with pressure alone to achieve the benefits of this invention. Similarly, many of

- 26 -

the rolls formed with continuous lengths of sheet/pplies  
utilizing thermoplastic resin systems can be treated with  
heat alone to achieve the benefits of this invention. It  
is preferred, however, to use both heat and pressure in  
5 treating the roll.

The number of sheets/layers forming the  
continuous length is unlimited as long as the length is  
sufficiently flexible to permit roll formation followed by  
molding/curing and unrolling, without adverse affect on  
10 utility. The flexibility of the treated lengths of the  
preferred embodiments of the present invention can be  
demonstrated by clamping a 30 cm square sample of the  
article horizontally along one side edge and measuring the  
amount of drape of the article (the amount of drape being  
15 measured by the distance between the level of the clamped  
side edge and the opposite edge). It is most preferred  
that the amount of drape be at least about 10 cm,  
preferably at least about 15 cm.

A molded roll 10 of the present invention is  
20 shown in FIGURE 1, wherein the continuous length/ply is  
designated by the numeral 11, and wherein the interleaf is  
designated by the numeral 12.

Studies of ballistic composites frequently  
employ a 22 caliber, non-deforming steel fragment of  
25 specified weight, hardness and dimensions (Mil-Spec.  
MIL-P-46593A(ORD)). The protective power of a structure  
is normally expressed by citing the impacting velocity at  
which 50% of the projectiles are stopped, and is  
designated the  $V_{50}$  value.

30 Usually, a composite armor has the geometrical  
shape of a shell or plate. The specific weight of the  
shells and plates can be expressed in terms of the areal  
density (ADT). This areal density corresponds to the  
weight per unit area of the structure. In the case of  
35 filament reinforced composites, the ballistic resistance  
of which depends mostly on the filament, another useful

- 27 -

weight characteristic is the filament areal density of composites. This term corresponds to the weight of the filament reinforcement per unit area of the composite (AD).

The following examples are presented to provide  
5 a more complete understanding of the invention.

#### EXAMPLE 1

A 0°/90° continuous cross ply about 54 inches (about 137 cm) wide is formed as previously described with two resin-impregnated networks. The networks comprise  
10 unidirectional high strength extended chain polyethylene filaments impregnated with a Kraton D1107 thermoplastic elastomer matrix (a polystyrene-polyisoprene-polystyrene-block copolymer having 14 weight percent styrene and a product of Shell Chemical). This filament, commercially  
15 available from Allied-Signal Corporation as SPECTRA® 1000, has a reported tenacity of 35 g/d, a reported modulus of 2000 g/d and a reported elongation of about 2.7 %. Denier is 650 and an individual filament denier is 5.4, or 120 filaments per yarn end. Filament size is about 27  
20 microns. The matrix material forms about 20% by volume and the filament about 80% by volume of the continuous ply.

The continuous cross ply/length is wound with a layer of Kraft paper into a roll with the Kraft paper separating successive wraps of the ply. This roll is  
25 placed in an oven at about 71°C. (about 160°F.), under no pressure, for four hours. The roll is then allowed to cool to room temperature (about 25°C.).

It is expected that the ballistic performance of the material will be good and that the material will  
30 drape like a fabric and handle easily.

#### EXAMPLE 2

A continuous cross ply is formed as in Example 1. An 0.5 mil linear low density polyethylene film (such as is produced by Raven Industries) is laminated to both  
35 sides of the ply, and the resulting length is wound with a layer of Kraft paper into a roll with the Kraft paper

- 28 -

separating successive wraps of the ply. This roll is placed in an oven, under no pressure, so that the center of the roll reaches a temperature of about 110°C. (about 230°F.), as measured with a thermocouple, for about one hour. The roll is then allowed to cool to room temperature (about 25°C.).

It is expected that the ballistic performance of the material will be good and that the material will drape like a fabric and handle easily.

10

EXAMPLE 3

Example 2 is repeated except that the roll is autoclaved at a temperature of about 121°C. (250°F.) for an hour at a pressure of approximately 120 lbs/in<sup>2</sup>.

It is expected that the ballistic performance of the material will be good and that the material will drape like a fabric and handle easily.

15

EXAMPLE 4

Example 2 is repeated except that the film which is laminated to both sides of the ply is an 0.35 mil film available from Raven Industries as a blend of Dowlex 2045-A, a linear low density polyethylene, and Attane 4001, an ethylene-octene copolymer.

It is expected that the ballistic performance of the material will be good and that the material will drape like a fabric and handle easily.

25

EXAMPLE 5

Example 4 is repeated except that the roll is autoclaved at a temperature of about 121°C. (250°F.) for an hour at a pressure of approximately 120 lbs/in<sup>2</sup>.

30

It is expected that the ballistic performance of the material will be good and that the material will drape like a fabric and handle easily.

EXAMPLE 6

A 0°/90° continuous cross ply is formed as in Example 1 except that the matrix used is a thermosetting resin, Derakane 8084 [an aqueous dispersion of

35

- 29 -

vinylester/styrene monomer (50/50 wt/wt) manufactured and sold by Dow Chemical, elongation about 10 to 12%, and it is put on with coating rollers to achieve about 20% by volume matrix and about 80% by volume filament in the continuous ply.

The continuous cross ply/length is wound with a layer of Kraft paper into a roll with the Kraft paper separating successive wraps of the ply. This roll is placed in an oven at about 105°C. (220°F.), without pressure, until the resin cures, about 20 minutes. The roll is then allowed to cool to room temperature (about 25°C.) prior to testing.

It is expected that the ballistic performance of the material will be good and that the material will drape like a fabric and handle easily.

#### EXAMPLE 7

A 0°/90° continuous cross ply is formed as in Example 1 except that the matrix used is a blend of a thermosetting resin Derakane 8084 (10% by weight) and a thermoplastic resin - Dispercoll E585 (10% by weight), an aqueous dispersion of a thermoplastic polyurethane, manufactured and sold by Mobay Corp. The matrix is put on with coating rollers to achieve about 20% matrix and about 80% filament in the cross ply.

The continuous cross ply/length is wound with a layer of Kraft paper into a roll with the Kraft paper separating successive wraps of the ply. This roll is placed in an oven at about 105°C. (220°F.), without pressure, until the resin cures, about 20 minutes. The roll is then allowed to cool to room temperature (about 25°C.) prior to testing.

It is expected that the ballistic performance of the material will be good and that the material will drape like a fabric and handle easily.

#### EXAMPLE 8

A 0°/90° continuous ply is formed and wound into a roll as in Example 1. A clear, heat shrinkable

- 30 -

polyester tape 5.1 cm (2 inches) in width and commercially available as Dunstone High Shrink Tape from Dunstone Corp. of Charlotte, North Carolina, is wound around the roll in a slightly overlapping spiral to completely wrap the roll. The wrapped roll is placed in an oven at about 71°C. (about 160°F.) for four hours. The tape shrinks with the heat to apply pressure to the roll. The roll is then allowed to cool to room temperature (about 25°C.) prior to testing.

It is expected that the ballistic performance of the material will be good and that the material will drape like a fabric and handle easily.

#### EXAMPLE 9

The procedure of Example 8 is repeated except that the wrapped roll is placed in an oven so that the center of the roll reaches a temperature of about 110°C. (about 230°F.), as measured with a thermocouple, for about one hour. The tape shrinks with the heat to apply pressure to the roll. The roll is then allowed to cool to room temperature (about 25°C.).

It is expected that the ballistic performance of the material will be good and that the material will drape like a fabric and handle easily.

25



- 31 -

## WE CLAIM:

1. A method of treating a continuous length comprising at least one uncured thermosetting resin-impregnated sheet, said length having a thickness and said thermosetting resin having an elongation such that said length of sheet is flexible when said thermosetting resin is cured, comprising the steps of:
  - a. winding said continuous length and a separation layer of a material into a roll with said layer separating successive wraps of said continuous length of sheet, said material being separable from said continuous length of sheet after said thermosetting resin is cured; and
  - b. curing the thermosetting resin.
2. The method of claim 1 wherein the thermosetting resin is selected from the group consisting of vinylesters, phenolics, epoxies, acrylics, urethanes, unsaturated polyesters and alkyds.
3. The method of claim 1 wherein the sheet is a network of filaments.
4. The method of claim 5 wherein the filaments have a tenacity equal to or greater than about 7 g/d, a tensile modulus equal to or greater than about 150 g/d and an energy-to-break equal to or greater than about 8 J/g.
5. The method of claim 5 wherein the filaments have a tenacity equal to or greater than about 22 g/d, a tensile modulus equal to or greater than about 900 g/d and an energy-to-break equal to or greater than about 27 J/g.
6. The method of claim 5 wherein the filaments are polyethylene filaments.
7. The method of claim 5 wherein the filaments are poly(p-phenylene terephthalamide) filaments.
8. The method of claim 1 wherein said curing step comprises exposing the roll to a temperature of about 20 to 150 °C. long enough to cure the resin without degrading the continuous length, and applying a pressure

- 32 -

of from about 10 psi (69 kPa) to about 10,000 psi (69,000 kPa) to the roll.

9. The method of claim 8 wherein the separation layer of material is a plastic film selected from the group consisting of polyester, polyethylene, polyvinyl chloride and ethylvinylacetate, whereby the pressure is applied when the plastic film shrinks from exposure to the temperature.

10. The method of claim 8 further comprising the step of wrapping the roll with a plastic wrap selected from the group consisting of polyester, polyethylene, polyvinyl chloride and ethylvinylacetate prior to the curing step, whereby the pressure is applied when the plastic wrap shrinks from exposure to the temperature.

11. A continuous length roll of sheet made according to claim 1.

12. A method of consolidating a continuous ply of at least two resin-impregnated sheets, comprising the steps of:

a. winding said continuous ply and a separation layer of a material into a roll with said layer separating successive wraps of said continuous ply; and

b. exposing said roll to a sufficient amount of heat to cause the resin-impregnated sheets to substantially adhere to one another, said material being separable from said continuous ply.

13. A method of consolidating a continuous ply of at least two resin-impregnated sheets, comprising the steps of:

a. winding said continuous ply and a separation layer of a material into a roll with said layer separating successive wraps of said continuous ply; and

b. exposing said roll to a sufficient amount of pressure to cause the resin-impregnated sheets to substantially adhere to one another, said material being separable from said continuous ply.

14. A consolidated roll made according to

- 33 -

claim 13.

15. A method of consolidating a continuous length comprising at least one resin-impregnated sheet and at least one sheet of film, comprising the steps of:

- 5       a. winding said continuous length and a separation layer of a material into a roll with said layer separating successive wraps of said continuous length of sheets; and
- 10       b. exposing said roll to a sufficient amount of heat and pressure to cause the resin-impregnated sheet and the sheet of film to substantially adhere to one another, said layer of material being separable from said continuous length.

1/1

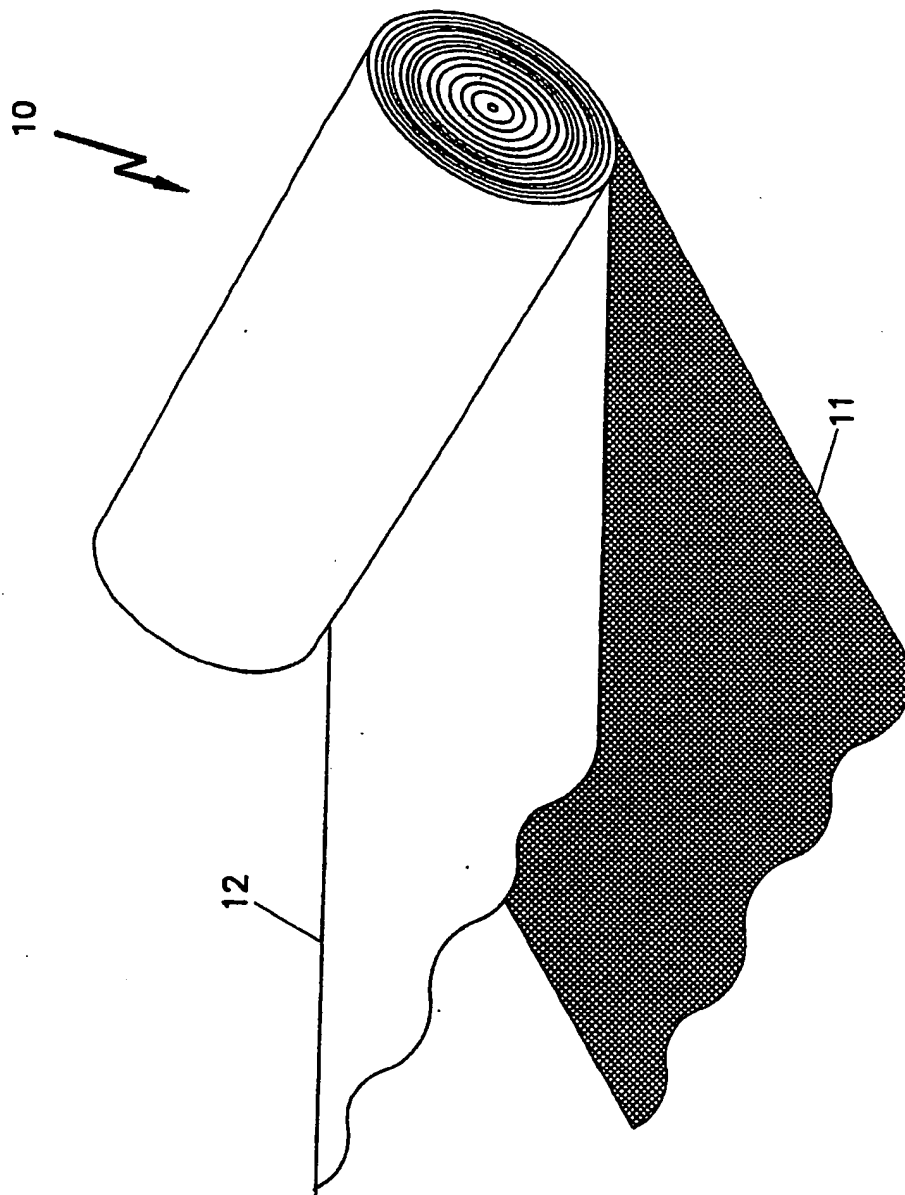


FIGURE 1

SUBSTITUTE SHEET

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/00463

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): B32B 31/20 U.S. Cl.: 156/323																				
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched <sup>4</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; text-align: left; border-bottom: 1px solid black;">Classification System <sup>1</sup></th> <th style="width: 70%; text-align: left; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">U.S.</td> <td style="padding: 5px;">156/323, 289, 85 428/906</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup></div>			Classification System <sup>1</sup>	Classification Symbols	U.S.	156/323, 289, 85 428/906														
Classification System <sup>1</sup>	Classification Symbols																			
U.S.	156/323, 289, 85 428/906																			
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup> <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <thead> <tr> <th style="width: 10%; text-align: left; padding: 5px;">Category <sup>6</sup></th> <th style="width: 60%; text-align: left; padding: 5px;">Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup></th> <th style="width: 30%; text-align: left; padding: 5px;">Relevant to Claim No. <sup>18</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X Y</td> <td style="padding: 5px;">US, A, 2,517,698 (MUSKAT) 08 August 1950 column 4, lines 6-18; column 6, lines 16-48 column 2, lines 40-54; column 3, lines 58-66, column 7, 2-22.</td> <td style="padding: 5px;">1-3, 11-14 1-6, 11-14</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X Y</td> <td style="padding: 5px;">US, A, 3,087,300 (ADLES) 02 May 1978 column 2, lines 27-37; column 3, lines 21-40</td> <td style="padding: 5px;">1-3, 15 8, 15</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4,235,574 (HARPELL ET AL.) 18 November 1986 column 2, lines 20-30, 47-59 column 7, lines 7-25.</td> <td style="padding: 5px;">1-6, 11-14</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4,125,423 (GOLDSWORTHY) 14 November 1978 column 10, lines 63-68 column 15, lines 26-53.</td> <td style="padding: 5px;">9, 10</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 3,767,500 (TALLY ET AL.) 23 October 1973</td> <td style="padding: 5px;">1-3, 11-14</td> </tr> </tbody> </table>			Category <sup>6</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>	X Y	US, A, 2,517,698 (MUSKAT) 08 August 1950 column 4, lines 6-18; column 6, lines 16-48 column 2, lines 40-54; column 3, lines 58-66, column 7, 2-22.	1-3, 11-14 1-6, 11-14	X Y	US, A, 3,087,300 (ADLES) 02 May 1978 column 2, lines 27-37; column 3, lines 21-40	1-3, 15 8, 15	Y	US, A, 4,235,574 (HARPELL ET AL.) 18 November 1986 column 2, lines 20-30, 47-59 column 7, lines 7-25.	1-6, 11-14	Y	US, A, 4,125,423 (GOLDSWORTHY) 14 November 1978 column 10, lines 63-68 column 15, lines 26-53.	9, 10	A	US, A, 3,767,500 (TALLY ET AL.) 23 October 1973	1-3, 11-14
Category <sup>6</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>																		
X Y	US, A, 2,517,698 (MUSKAT) 08 August 1950 column 4, lines 6-18; column 6, lines 16-48 column 2, lines 40-54; column 3, lines 58-66, column 7, 2-22.	1-3, 11-14 1-6, 11-14																		
X Y	US, A, 3,087,300 (ADLES) 02 May 1978 column 2, lines 27-37; column 3, lines 21-40	1-3, 15 8, 15																		
Y	US, A, 4,235,574 (HARPELL ET AL.) 18 November 1986 column 2, lines 20-30, 47-59 column 7, lines 7-25.	1-6, 11-14																		
Y	US, A, 4,125,423 (GOLDSWORTHY) 14 November 1978 column 10, lines 63-68 column 15, lines 26-53.	9, 10																		
A	US, A, 3,767,500 (TALLY ET AL.) 23 October 1973	1-3, 11-14																		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>*</sup> Special categories of cited documents: <sup>16</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>																				
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">           Date of the Actual Completion of the International Search <sup>1</sup>             26 March 1991             International Searching Authority <sup>1</sup>             ISA/US         </td> <td style="width: 50%; padding: 5px;">           Date of Mailing of this International Search Report <sup>2</sup>   <div style="text-align: center; font-size: 1.2em; font-weight: bold;">18 APR 1991</div> <div style="text-align: center;">            Signature of Authorized Officer <sup>20</sup>            Daniel J. Stemmer         </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <sup>1</sup>  26 March 1991  International Searching Authority <sup>1</sup>  ISA/US	Date of Mailing of this International Search Report <sup>2</sup>  <div style="text-align: center; font-size: 1.2em; font-weight: bold;">18 APR 1991</div> <div style="text-align: center;">            Signature of Authorized Officer <sup>20</sup>            Daniel J. Stemmer         </div>																
Date of the Actual Completion of the International Search <sup>1</sup>  26 March 1991  International Searching Authority <sup>1</sup>  ISA/US	Date of Mailing of this International Search Report <sup>2</sup>  <div style="text-align: center; font-size: 1.2em; font-weight: bold;">18 APR 1991</div> <div style="text-align: center;">            Signature of Authorized Officer <sup>20</sup>            Daniel J. Stemmer         </div>																			

Form PCT/ISA/210 (second sheet) (May 1986)

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**